Abstract

***Title:* Investigation of multiferroic properties of graphene and oxide multiferroic systems for spintronics applications**

Because of tremendous application potential in the area of spintronics and intense research during the last two decades, the magnetoelectric (ME) multiferroic materials could create a new genre in condensed matter physics. In the era of information storage and logic devices, spintronics has opened a new vista and the ME materials have enriched this field by utilizing the control over electron's spin or magnetic moment by external electric field. An ideal spin channel solid state material must also have large spin-orbit coupling (SOC) along with long spin diffusion length. It appears that, in spite of some limitations, Bismuth Ferrite ($BiFeO_3$) and graphene – as ME and spintronics systems – could offer potentially superior properties suitable for different spintronics applications. Graphene exhibits longer spin relaxation time with long spin diffusion lengths of several micrometres but it produces weak spin-orbit coupling. $BiFeO_3$, a well known perovskite, is the most popular room temperature ME system. But due to small carrier velocity, spin diffusion length is limited in $BiFeO_3$. In recent time, it has been demonstrated, using first principles calculation, that large spin diffusion length and carrier mobility in graphene helps in improving the magnetization in $BaMnO_3$/graphene system with C-Mn bonding at the interface [Sci. Rep. **6**, 31346 (2016)]. This article intrigued and encouraged us to combine graphene and $BiFeO_3$. We, therefore, explored here graphene/ $BiFeO_3$ system in various forms (nano-composite and hetero-structure) which produces different types of interfaces. Of course, in the last decade, extensive research has been carried out to examine the functional properties (magnetization, spin-polarized charge conduction etc) of graphene in graphene/$BiFeO_3$ hetero-structures. But the reverse scenario i.e., how the ME properties $BiFeO_3$ could be influenced and even improved because of 'proximity' of graphene (and, thereby, development of superior ME nano composite or hetero-structure) has not been studied by the research community so far. Given this backdrop, we focused, in the work being presented in this thesis, on the influence of graphene or its derivatives (mainly reduced graphene oxide [rGO]) upon the crystallographic and physical properties of $BiFeO_3$. We opted for two systems- (i) nano composite of rGO and $BiFeO_3$, and (ii) hetero-structure of rGO and $BiFeO_3$ thin film. In the study of nano-composites, we successfully synthesized two types of samples – (i) one with Fe-C covalent bonding, and (ii) another with only Van der Waals bonds. We observed moderate to significant changes in the crystallographic structure, electrical, magnetic, and magnetoelectric properties as a result of presence of Van der Waals or covalent bonds at the interface. Interestingly, the presence of covalent Fe-C bonds at the interface appears to have influenced the surface magnetocrystalline anisotropy and its magnetic-field dependence significantly. As a result, the bulk and surface magnetostriction versus magnetic field patterns follow opposite trends. This, in turn, results in non-monotonic magnetic-field dependence of remanent ferroelectric polarization. In the pure $BiFeO_3$ system, the pattern is monotonic. The hetero-structure of rGO/$BiFeO_3$ thin films too, exhibited changes in the properties of $BiFeO_3$ because of 'proximity' of rGO. They were synthesised using inexpensive solution deposition techniques. We also attempted to synthesize highly ferromagnetic $BiFeO_3$ as well as graphene. For this, we successfully introduced new chemical route to make silver (Ag) wrapped self-assembly of $BiFeO_3$ nano chains. This new $BiFeO_3$/Ag nano-composite exhibited more than an order of magnitude jump in saturation magnetization at room temperature. Next, we modified the diamagnetic single layer graphene to ferromagnetic graphene by hydrogenation and also established a new solution chemistry path to easily dehydrogenate them via oxidation reaction. Thus, we noticed reversibility in magnetic as well as electrical properties in graphene.

In this work, we have integrated rGO and $BiFeO_3$ in various forms (nano composite and hetero-structure) containing different interfaces (bonded and non-bonded) using inexpensive chemical routes. We observed novel changes in the ME properties of $BiFeO_3$ and tried to explore the underlying physics. These results could trigger engineering of newer classes of magnetoelectric materials by combining graphene and other single-phase multiferroic systems for a plethora of applications in spintronics.

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